

# **Pilot Organophosphorus Pesticide Air Monitoring Project**

## **FINAL SAMPLING PLAN**

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### **1. PURPOSE**

In April 2007 the Washington State Legislature requested an “examination of airborne pesticide concentrations in agricultural areas of the state.” The University of Washington’s Department of Environmental and Occupational Health Sciences (UW-DEOHS) was assigned the task of monitoring organophosphorus (OP) pesticides in agricultural regions of Washington State. UW-DEOHS will measure air concentrations of OP pesticides used in Washington agriculture during the 2008 growing season. The purpose of this monitoring is to examine whether off-target movement of OP pesticides during and following pesticide applications poses a potential risk to residents or bystanders.

#### **1.1 Budget**

The University of Washington submitted a fiscal note in February 2007 at the request of the state legislature. The UW fiscal note requested \$289,000 in direct costs to conduct this project. UW also agreed to waive all indirect costs for the project. The Department of Health awarded the University of Washington a contract of \$250,000, resulting in a 13.5% reduction in available resources for the project. Further budget information is available upon request.

#### **1.2 Target Chemical Selection**

We plan to use the limited resources available to focus on OP pesticide applications that have relatively high toxicity, are in common use, and for which there has been little or no previous community air monitoring in Washington. We consulted U.S. Environmental Protection Agency information on acute and chronic toxicity; the Pesticide Incident Report and Tracking Panel reports for information on OP pesticide-related illnesses in the state; data from the National Agricultural Statistical Service to determine the most commonly used OP pesticides in the state; and a review of the existing literature to determine prior air monitoring of OP pesticides in the state. We also considered the physical characteristics of the compounds and the manner of their application. We concluded that orchard power blast applications of chlorpyrifos, (the active ingredient of Lorsban™) and azinphos-methyl (the active ingredient of Guthion™) were of highest priority. We did not prioritize malathion due its relatively low mammalian toxicity; we did not prioritize phosmet due to its low toxicity relative to azinphos-methyl; we did not prioritize aerial applications of methamidophos on potatoes, since an earlier study suggests that off-target

concentrations following such applications are probably not a significant health risk for nearby communities (Ramaprasad et al., 2008).

### **1.3 General Design**

We plan to conduct sampling in two phases. Phase 1 will focus on the late winter or early spring dormant airblast applications of OP pesticides on tree fruit. The target compound for Phase 1 will be the OP pesticide, chlorpyrifos. Phase 2 will focus on the late spring and early summer orchard spraying for codling moth control. The target compound for Phase 2 will be the OP pesticide, azinphos-methyl. The sampling strategy outlined below for Phase 1 will be duplicated for Phase 2.

## **2. PHASE 1 SAMPLING STRATEGY: CHLORPYRIFOS APPLICATIONS**

Our sampling strategy for the measurement of chlorpyrifos air concentrations is outlined in Table 1.

### **2.1 Regions**

We plan to sample in two tree fruit regions of Washington State where chlorpyrifos applications typically occur: the Yakima Valley and the greater Wenatchee area. The lower Columbia River valley was considered, but this was not possible logistically, since spraying in that region usually begins earlier than in the other regions. The appendix provides a chlorpyrifos and azinphos-methyl use-density maps for the Yakima and Wenatchee regions. The maps were developed by our research team using data from the WA Department of Agriculture, the National Agricultural Statistical Service, and the U.S. census. A description of the method used to develop the maps is included in the appendix.

### **2.2 Sample Types**

We intend to collect three types of samples: near-field receptor; ambient community; and near-field perimeter. Collection of each of these types of samples requires a different sampling strategy, as outlined below.

#### **2.2.1 Near-Field Receptor Sampling**

The purpose of near-field receptor sampling is to determine chlorpyrifos air concentrations at locations where people live or spend significant amounts of time, and to produce data sufficient to evaluate the risk for sub-acute exposures.

Sampling sites will be selected in cooperation with farm worker and other residential community members. We will identify locations that are believed to receive relatively high chlorpyrifos exposures during airblast applications on tree fruit. We will then place samplers in that location to capture the concentration of chlorpyrifos that might be encountered by individuals living at or frequenting these locations. We will collect two 24-hour samples each day for 28 days at each of three sampling sites in each region to characterize potential bystander exposure. Two quality assurance air samples will be collected at one site in each region concurrent with the other samples.

The near-field receptor site criteria are as follows: less than 100 meters from a crop associated with chlorpyrifos power blast applications; secure (fenced and locked or not readily accessible to the public); access seven days per week for 28 days; outdoor AC 110 power outlet; low foot traffic; not a pet area or play area; no vehicle traffic; samplers located 1-2 meters from the ground; sampler distance from buildings, walls or solid fences at least one-half the height of structure.

### **2.2.2 Ambient Community Sampling**

The purpose of ambient community sampling is to determine the exposure potential for the general population in the study area, and to provide a reference value for the other data collected in the study.

We will collect one 24-hour ambient community sample each day in each region over the 28-day study period. The ambient sampler will be located in a nearby community to determine air concentrations distant from the application site. Prior experience and dispersion modeling results from other studies suggest that the ambient community monitoring locations should be located at least one-half kilometer from the nearest applied fields. Previous sampling in a Washington agricultural region (Tolbert et al. 2008) indicated that ambient community air can be considered reasonably well mixed on a scale of five to ten kilometers.

The ambient community site criteria are as follows: at least one-half kilometer (500 meters) from from a crop associated with chlorpyrifos power blast applications; secure (fenced and locked or not readily accessible to the public); access 24 hours per day and 7 days per week for 28 days; outdoor AC 110 power source.

### **2.2.3 Near-Field Perimeter Sampling**

The purpose of near-field perimeter sampling is to determine chlorpyrifos air concentrations at the edge of an application site, and to produce data sufficient to evaluate the risk for acute exposures.

We will conduct near-field perimeter sampling at two sites. These sites will be selected in cooperation with the grower community. The grower will provide information regarding the application rate, the duration of application, the total amount of active ingredient applied, and other information relevant to an emission rate estimate. We plan to attach a global positioning system (GPS) unit to the spray tractor to document its movement. We will also collect on-site meteorological information throughout the sampling period. The combination of this information will allow us to construct a model of off-target pesticide movement.

We will conduct near-field perimeter sampling following the approach used by the California Air Resources Board. A four day sampling schedule will be used for each region: pre-spray day; spray day; post-spray day 1; post-spray day 2.

On the pre-spray day 12 to 24-hour samples will be collected at four locations around the perimeter of the orchard block to be sprayed. On the spray day and on the first post-spray day three consecutive approximate 8-hour samples (for a total of 24 hours) will be collected at eight locations. On the second post-spray day, 12 to 24-hour hour samples will be collected at the eight locations. The eight-hour samples will take place at approximately 6:00-14:00, 14:00-22:00, and 22:00-6:00). Each day two quality assurance samples will be collected at each site as per the sample schedule for that day.

The near-field perimeter site criteria are as follows: well-defined orchard block that can be treated in one day by a single applicator; access 24 hours per day for the 4-day study period; use of power blast application equipment; no drift retardant used during applications; secure; use of generators 24 hours per day acceptable to property owners and neighbors; at least 100 meters from other orchards that will be treated with chlorpyrifos during the study period.

### **3. PHASE 2 SAMPLING STRATEGY: AZINPHOS-METHYL APPLICATIONS**

The target compound for Phase 2 sampling will be azinphos-methyl and phosmet.. The temporal sampling frame is expected to be mid-May through early July. We intend to use the sampling strategy for Phase 2 that we have outlined for Phase 1. Any proposed modifications in the sampling plan for Phase 2 will be discussed with the Department of Health and its Technical Review Panel.

### **4. SAMPLING METHODS**

#### ***4.1 Meteorological Data***

A portable meteorological station will be run continuously throughout the sampling period at each of the near-field perimeter sampling sites to monitor local weather conditions such as temperature, pressure, rainfall, wind speed and wind direction. Local weather data will be collected in association with the near-field receptor and ambient community sampling.

#### ***4.2 OP Pesticide Sampling***

Sampling for chlorpyrifos will be performed according to methods presented in the National Institute for Occupational Safety and Health (NIOSH) Method 5600, OP Pesticides, and similar to those used by the California Air Resources Board, as summarized by Baker et al. (1996). Near-field perimeter samples will be collected at 6 liters per minute using glass Occupational Safety and Health Administration Versatile Sampler (OVS) tubes. Near-field receptor and ambient community sampling will use the same tubes and a flow-rate of 2 liters per minute. The sampling tubes contain two sections of XAD®-2 sorbent material preceded by quartz particulate matter filters. Calibrated rotameters will be used to measure sample flow rates at the start and end of each sampling period. Sampling tubes will be placed one to two meters above ground level to avoid contamination from ground sources and will be covered to shield from sunlight and rain. Samplers will be placed at a distance from obstructions according to the following formula used by the California Air Resources Board: place the sampler at a distance from the obstruction that is at least one-half the height of the obstruction. Duplicate samples will be collected at each sample location and on every sampling day. Field spikes and blanks representing the equivalent of 10% of the samples collected will be prepared and analyzed for quality assurance purposes. Standard operating procedures (SOPs) for the field sampling and QA/QC sampling are available upon request.

#### ***4.3 Sample Handling***

All sorbent tubes will be handled with nitrile gloves, capped, and stored individually in sealed plastic bags on ice in an insulated ice chest immediately following sample collection and during transport from the site of collection to a field transfer station. Upon arrival samples will be removed from the ice chest and stored at approximately -20 °C pending transfer to the University of Washington's Environmental Health Laboratory and Trace Organics Analytical Center for pesticide analysis.

#### ***4.4 Sample Analysis***

Samples will be analyzed at the University of Washington Environmental Health Laboratory. This laboratory is AIHA certified, and has many years of experience in the analysis of environmental samples containing pesticides. We expect the laboratory to follow NIOSH Method 5600: i.e., samples will be extracted using a toluene/acetone solution and analyzed by gas chromatography using a flame photometric detector. To attain lower detection limits the laboratory may modify NIOSH Method 5600 procedures. A full report providing the laboratory

procedures will be submitted to the Department of Health as part of the University of Washington's Analytical Plan.

## **5. SAMPLING PLAN RATIONALE**

The proposed sampling plan seeks community stakeholder support from both growers and farm workers to achieve the study aims. Both community groups will be engaged to identify specific sample sites. The approach described above will sample a range of data sources and strikes a balance between a monitoring plan that closely follows a known spray and a monitoring plan that strictly samples receptor locations without regard to the conditions or timing of events at the applied fields. This sampling plan will provide measurements of actual community exposures, and will also provide a basis for estimating the upper range of exposure that may occur near applied fields.

The near-field receptor sample locations will provide air concentration data near crops that are likely to be sprayed with chlorpyrifos. Washington State does not require pesticide use reporting, so we may be unable to confirm specific information on applications to nearby crops. This sampling will be conducted so as to respect the privacy and/or wishes of community members to remain anonymous. The near-field receptor locations will allow the study team to establish a range of exposures that occur in community areas near commonly treated crops during the peak spraying time when multiple orchards may be sprayed concurrently or consecutively.

The near-field perimeter sample locations will provide air concentration data immediately adjacent to known chlorpyrifos-treated orchards. Additional data such as the application rate, timing of the application, position and characteristics of the sprayer will be available by engaging grower cooperation. This information will allow the study team to accurately measure and model the spray event and post-application emissions based on the source conditions and on-site meteorology. These measurements can provide an assessment of the upper range for potential pesticide exposures, and will serve as the basis of a modeling tool for estimating the range of exposures in nearby communities under a variety of application and weather scenarios. The monitoring will strive to capture the air concentrations near a sprayed field on a typical day and for several days post spray. We recognize that prior knowledge of the monitoring potentially could affect measurements during applications, but obtaining accurate spray information during the application removes a large uncertainty in the data collection. We believe that post-application volatilization is unlikely to be affected by prior notification, since this largely depends on the local meteorology, which is beyond the grower's control.

## **6. REFERENCES**

- Baker LW, Fitzell DL, Seiber JN, Parker TR, Shibamoto T, Poore MW, Longley KE, Tomlin RP, Propper R, Duncan DW. 1996. Ambient air concentrations of pesticides in California. *Environ Sci Technol* 30:1365-1368.
- Ramaprasad J, Yost MG, Fenske RA et al. 2008. Children's Inhalation Exposure to Methamidophos from Sprayed Potato Fields in Washington State: Exploring the Use of Probabilistic Modeling of Meteorological Data in Exposure Assessment. Submitted to the *Journal of Exposure Science and Environmental Epidemiology*.
- Tolbert LA, Yost MG, Kissel JC, Galvin K, Fenske RA. 2008. Ambient air concentrations of organophosphorus pesticides due to volatilization during seasonal pesticide applications. Manuscript in preparation. (See also M.S. Thesis by Lisa A. Tolbert, University of Washington Department of Environmental and Occupational Health Sciences, 2007)

**Table 1.** Phase 1 sampling strategy for measurement of chlorpyrifos air concentrations associated with orchard spraying in Yakima and Wenatchee regions

<b>Receptor Samples</b>	Within 100 meters of orchard land
Time frame	28 days to capture chlorpyrifos spray
Number of sites per region	3
Number of air samples per site	2 per day
Sample duration	24-hour
Sample flow rate	2 liters per minute
Quality assurance air samples	2 per day at one site in each region
Total air samples	336 (168 per region)
QA air samples	112 (56 per region)
Field spikes and blanks	45 (additional 10%)
<b>Total Receptor Samples</b>	<b>493</b>
<b>Ambient Samples</b>	At least 500 meters from orchard land
Time frame	28 days to capture chlorpyrifos spray
Number of sites per region	1
Number of air samples per site	2 per day
Sample duration	24-hour
Sample flow rate	2 liters per minute
Quality assurance air samples	none
Total air samples	112 (56 per region)
Field spikes and blanks	11 (10% additional)
<b>Total Ambient Samples</b>	<b>123</b>
<b>Perimeter Samples</b>	Within 15 meters of sprayed orchard
Time frame	4 days to capture chlorpyrifos spray
Number of sites per region	1
<i>Pre-spray day samples</i>	
Number of air samples per site	8
Sample duration	12 to 24-hour
Sample flow rate	6 liters per minute
Quality assurance air samples	2 at each site
<i>Spray day samples</i>	
Number of air samples per site	16
Sample duration	3 8-hour time periods
Sample flow rate	6 liters per minute
Quality assurance air samples	2 at each site for each time period
<i>Post-spray: day 1 samples</i>	
Number of air samples per site	16
Sample duration	3 8-hour time periods
Sample flow rate	6 liters per minute
Quality assurance air samples	2 at each site for each time period
<i>Post-spray: day 2 samples</i>	
Number of air samples per site	16
Sample duration	12 to 24-hour
Sample flow rate	6 liters per minute
Quality assurance air samples	2 at each site
Total air samples	272 (136 per site)
Field spikes and blanks	27 (10% additional)
<b>Total Perimeter Samples</b>	<b>297</b>
<b>Total Phase 1 Air Samples</b>	<b>913</b>